Kinetics of Self-Poisoning of Pd/Al₂O₃ Catalysts in the Hydrogenolysis of Cyclopentane: Influence of the Dispersion of Palladium and Sulfate Poisoning

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The deactivation of Pd/Al₂O₃ catalysts occurring in the course of cyclopentane hydrogenolysis has been examined. The decay of catalytic activity can be represented by the theoretical model proposed by Levenspiel [*J. Catal.* **25**, 265 (1972)]. The influence of sample weight, reactant pressure, and temperature can then be rationalized. The deactivation constant measured by this procedure is found to be independent of the dispersion of palladium. Therefore deactivation, like hydrogenolysis of cyclopentane on palladium, is not sensitive to particle size effects. However, both reactions are poisoned by sulfate when the reduction is carried out at 400°C.

NOMENCLATURE

a = activity defined as the ratio of the reaction rate at time t to the reaction rate at time zero.

A = gas-phase reactant.

C = concentration (moles per liter).

k = rate constant for the main reaction (hydrogenolysis).

k_d = rate constant for the deactivation reaction.

$k'_d = k_d \times (C_A)^p$

k_e = experimental rate constant of deactivation (slope of the linearized plot of activity as a function of time)

p = order of concentration dependence of the deactivation.

$-r_A$ = rate of reaction of A.

W = weight of catalyst.

X_A = fractional conversion of A.

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F_{A_0} = feed rate of reactant A.

t = time.

INTRODUCTION

Catalyst deactivation is an important factor in industrial practice and has been the object of renewed attention in recent years (*1*). Szepe and Levenspiel (*2*) developed a general mathematical structure for describing the kinetics of catalytic reactions affected by deactivation, and Levenspiel (*3*) discussed the limitations of several types of reactors for the determination of the orders of reaction and deactivation. Khang and Levenspiel (*4*) tested how a simple rate law of deactivation could be affected by the complex interaction of pore diffusion resistance and reaction kinetics on a catalyst pellet. Later, Wolf and Petersen (*5*) applied the steady-state approximation to analyze self-poisoning reactions in an effort to clarify the mechanism of poisoning.

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Thus there is already some theoretical basis which can be confronted with experimental results in order to test its validity. Self-poisoning of supported metallic catalysts can occur by several processes, catalyzed either by the metal or the support, and a possibility exists that the simplified models used in theoretical calculations are in contradiction with experimental work. A simple reaction was therefore needed. Hydrogenolysis of cyclopentane on palladium catalysts was chosen as the model reaction since a previous study (6) had shown that the catalytic activity per surface palladium atom was constant for Pd/Al_2O_3. This can be considered as good evidence that the reaction is restricted to the metal.

The aspects investigated in this work are the kinetics of deactivation, and the influence of metallic dispersion and of poisons on deactivation.

EXPERIMENTAL

Catalysts. A series of palladium catalysts was prepared by the ion-exchange technique (7). Alumina was contacted overnight with an acidic solution of $PdCl_2$ then filtered and dried at 110°C.

The supports were: (i) Degussa alumina (grade 110°C), nonporous; surface area, 180 m²/g; and (ii) γ-alumina prepared in the laboratory by calcining bayerite at 500°C; surface area, 320 m²/g. For sulfate poisoning the γ-alumina support was first impregnated by known amounts of $(NH_4)_2SO_4$.

A good dispersion of palladium (90–100%) was obtained after a calcination at 400°C in oxygen and reduction in dry hydrogen at 300°C. Changing the temperature of calcination and reduction resulted in gradual sintering of the metallic phase, probably via the variation of the water content of the sample as proposed by Dalla Betta and Boudart (8).

The metallic dispersion was measured by the classical H_2–O_2 volumetric titration proposed by Benson *et al.* (9). Hydrogen was adsorbed at 70°C under a low pressure ($p < 1$ Torr) to avoid dissolution in the bulk. Oxygen was adsorbed at room temperature. The dispersion of palladium is defined in the usual way as the ratio of the number of surface palladium atoms which adsorb hydrogen or oxygen to the total number of palladium atoms of the sample. The results of chemisorption measurements were compared with those obtained from electron microscopy determination of the distribution of particle sizes and a good agreement was observed.

Materials. Cyclopentane for spectroscopy (purity, $\simeq$99.7%) from Merck was used as reactant without further purification.

Apparatus and procedure. A continuous flow microreactor was used at low conversion, less than 2%, to minimize heat and mass transfer limitations. Catalytic activities were determined on an aliquot of the sample used for dispersion measurements. The sample was reactivated for 1 hr at 300°C in flowing hydrogen. The reaction was performed at 290°C using a partial pressure of hydrocarbon of 100 Torr and a partial pressure of hydrogen of 660 Torr. The catalytic activity was measured for 3 hr at least at intervals of 15 min. On-stream gas chromatographic analysis was used. The sole product of hydrogenolysis in the gas phase was *n*-pentane.

The importance of diffusional limitations may be estimated by applying the criterion of Weisz (10) to the experimental results. The highest rate of reaction at 290°C was 8.10^{-7} mol/s/g, when using a partial pressure of cyclopentane of 100 Torr and a grain size of catalyst lower than 10^{-1} cm. According to Weisz (10), the effective diffusity D_{eff} will have an approximate value of 10^{-3} cm²/sec. Taking $\rho = 0.6$ cm³/g for the density, we can calculate the factor Φ as:

$$\Phi = \frac{R^2\rho}{D_{eff}C_A}\left(-\frac{dn_A}{mdt}\right) = 0.25.$$

$\Phi < 1$ ensures an effectiveness factor close to 1, and diffusional limitations are not important at 290°C. However, they may play a role at higher temperatures.

RESULTS AND DISCUSSION

1. Kinetics of Deactivation

Palladium catalysts deactivate steadily at 290°C. The catalytic decay obeys the hyperbolic law first proposed by Germain and Maurel (11), as exemplified in Fig. 1.

The hyperbolic law is a particular form of a more general rate law proposed by Szepe and Levenspiel (2). The fundamental assumption of this formalism is that deactivation and rate laws are separable. The physical meaning of that assumption
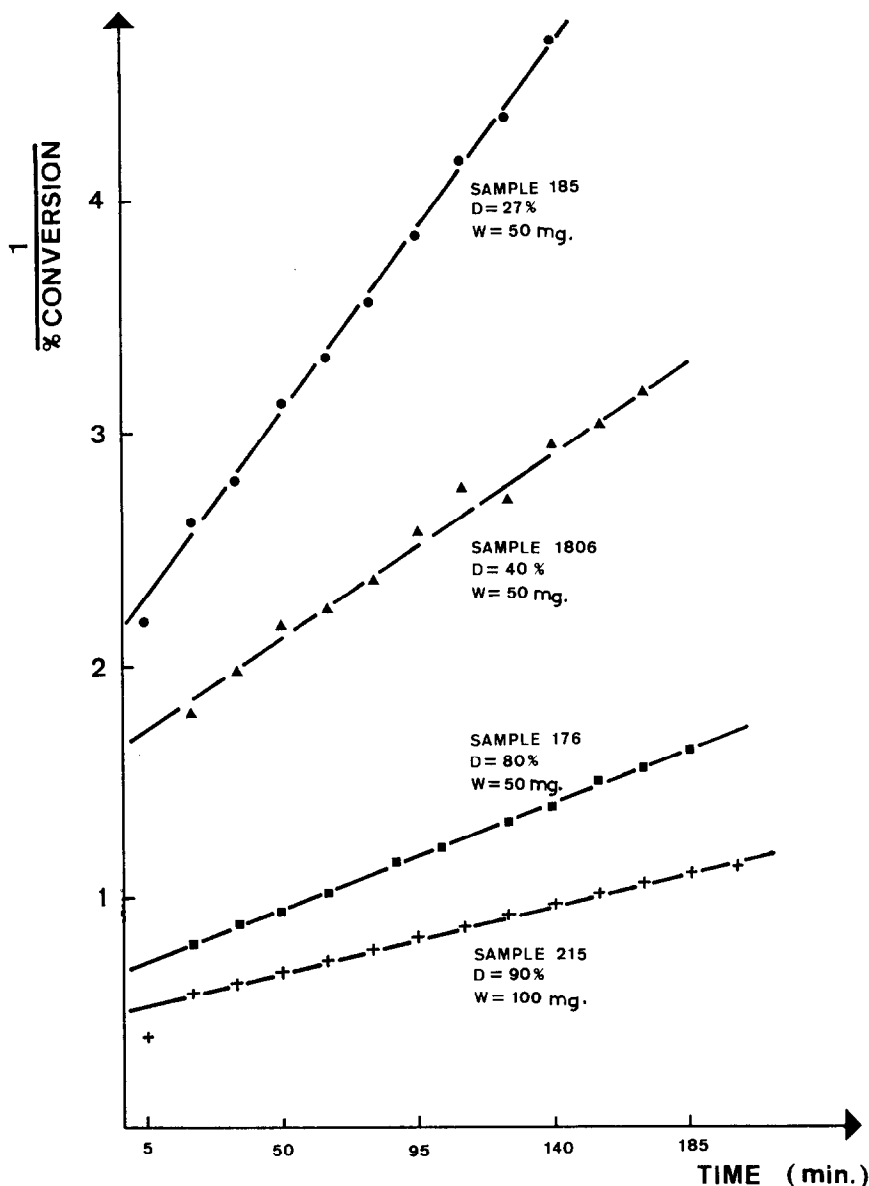

FIG. 1. Deactivation of some Pd/Al$_2$O$_3$ samples plotted using the homographic law. Temperature, 290°C; flow rate, 0.3 cm^3/sec; pressure of cyclopentane, 100 Torr.

TABLE 1

Influence of the Sample Weight on the Slope of the Deactivation Law[a]

Sample	Weight (g)	F_{A_0} ($10^6 \cdot$ mol/s)	Initial activity (mol/s·g of Pd·10^5)	k_e	$\dfrac{k_e \cdot W}{F_{A_0}} \times 10^3$	Percentage conversion at $t = 0$
Al$_2$O$_3$-218	0.05	1.8	1.5	0.018	0.5	0.2
	0.10	1.8	1.8	0.010	0.55	0.5
SiO$_2$-71	0.05	1.8	4.0	0.008	0.22	1.1
	0.10	1.8	4.0	0.004	0.22	2.2
Al$_2$O$_3$-173	0.05	1.8	3.9	0.009	0.25	1.08
	0.10	1.8	3.9	0.005	0.27	2.08
	0.15	3.6	3.86	0.073	0.30	1.61

[a] Temperature, 290°C; pressure of cyclopentane, 100 Torr.

is that coke affects the local properties but has no long-range effect.

Self-poisoning is generally represented as a parallel reaction of hydrogenolysis, and therefore the formal scheme:

$$\text{cyclopentane} \begin{array}{c} \nearrow \;\; n\text{-pentane} \\ \\ \searrow \;\; \text{coke} \end{array}$$
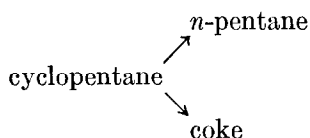
can be applied.

According to Levenspiel et al. (2, 3) we can write:

$$-r_A = k \cdot a$$

for the reaction rate, and

$$-\frac{da}{dt} = k_d a^m (C_A)^p = k'_d a^2$$

for the deactivation rate, taking into account that the experimental results show that the reaction order relative to cyclopentane is zero and that a homographic decay corresponds to $m = 2$.

A differential reactor at low conversion can be considered as a well mixed reactor, and therefore the reaction rate is:

$$\frac{W}{F_{A_0}} = \frac{X_A}{-r_A} = \frac{C_{A_0} - C_A}{k \cdot a C_{A_0}}.$$

A simple calculation gives:

$$\frac{W}{F_{A_0}} = \frac{C_{A_0} - C_A}{k C_{A_0}} + \frac{C_{A_0} - C_A}{k C_{A_0}} \cdot k'_d t,$$

the equation previously proposed by Levenspiel (3) for this particular case and which will be applied to the experimental results.

A plot of the reciprocal conversion against time gives the experimental constant of deactivation, k_e, the slope of the homographic plot, which can therefore be written:

$$k_e = \frac{k_d}{k} (C_A)^p \frac{F_{A_0}}{W}.$$

One obvious consequence of this formulation is that the mass of catalyst, the

TABLE 2

Influence of the Partial Pressure of Cyclopentane on the Slope of the Deactivation Plot and Initial Catalytic Activity[a]

Partial pressure (Torr)	Concentration of reactant (mol/liter)	$k_e \cdot 10^4$	Initial activity (mol/s·g of Pd·10^5)	$\dfrac{k_e}{C_A^2}$
26	0.0017	8	2.33	277
47	0.0029	17	2.35	202
63	0.0038	32	1.73	222
100	0.0059	88	3.00	253

[a] Temperature, 290°C; weight of sample, 50 mg; catalyst, sample 184 with 1% Pd.

reactant pressure and the metallic area, which is included in k, will influence the observed slope of the deactivation line.

The influence of the weight of sample is illustrated in Table 1: k_e is indeed inversely proportional to the mass, in agreement with the theoretical model.

Changing the reactant pressure also changes the deactivation constant. For pressures of cyclopentane less than 200 Torr the homographic law fits the data well. The values obtained for the experimental constant k_e, as a function of the

partial pressure, are given in Table 2: k_e increases when the pressure increases, while the initial activity remains approximately constant. The order relative to cyclopentane is therefore zero for the reaction rate, while a second order is found for deactivation at 290°C.

The influence of temperature is more complex. When increasing the reaction temperature several possibilities appear:

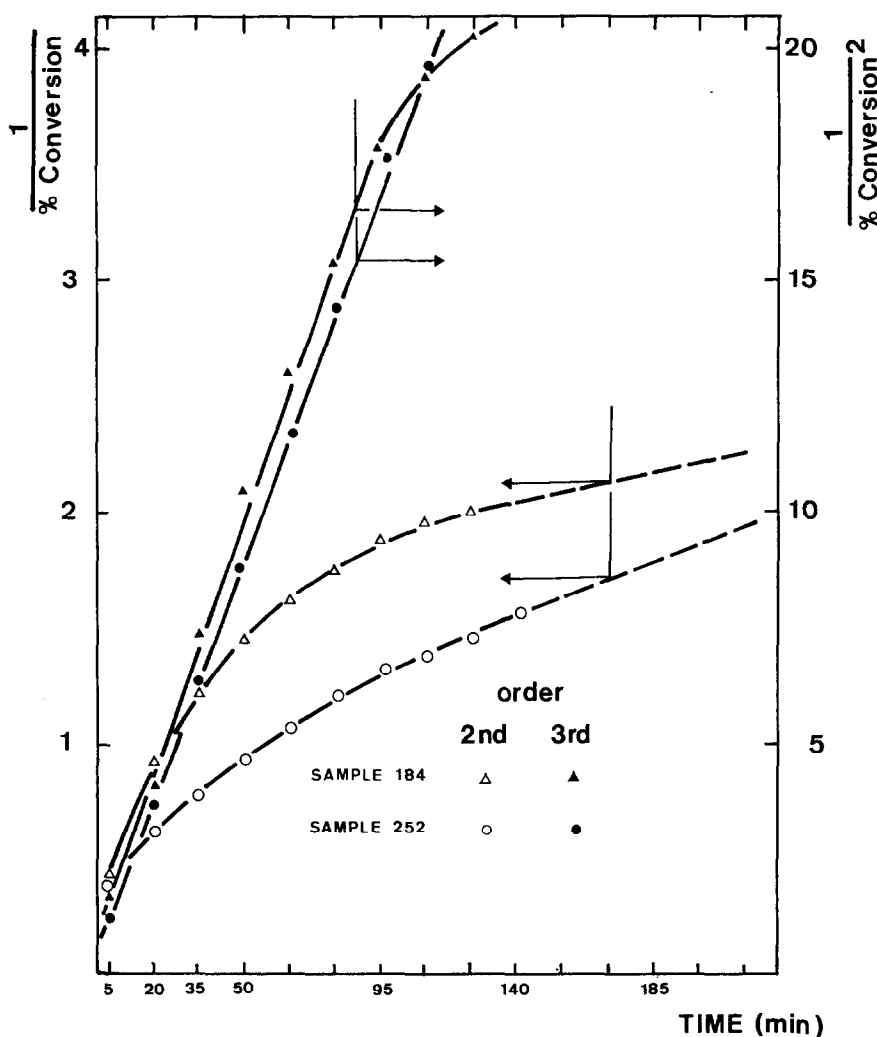(a) The deactivation mechanism is not changed and the homographic law is still

Fig. 2. Plots of third-order and second-order deactivation law for catalyst decay at 320°C.

valid. In such a case it is possible to measure the deactivation constant and find a deactivation energy. The fact that log k_e vs reciprocal temperature yields a straight line can be considered as a good test of the internal consistence of the results.

The apparent activation energy is 23 kcal/mol. The activation energy found for hydrogenolysis is 40 kcal/mol, in good agreement with literature data (12); therefore the true activation energy of the deactivation process can be estimated as 63 kcal/mol. Rostrup–Nielsen (13) reports an apparent activation energy for coking of supported nickel by n-heptane + water of 40 kcal/mol.

(b) The deactivation mechanism may change at higher temperatures ($T = 320°C$) on the most active catalysts because of diffusional limitations. A third-order law in function of time ($-da/dt = k_d a^3$) is then observed as foreseen by Khang and Levenspiel (4). After a certain time (Fig. 2) the law shifts to a homographic one, which reflects the fact that the reaction rate is now lower than the rate of diffusion.

The model proposed by Levenspiel is therefore in good agreement with the experimental results obtained on that catalytic system. A consequence of this conclusion is that it appears possible to measure a rate constant of deactivation which will be characteristic of that reaction, and which is independent of the metal area.

2. Influence of the Dispersion of Palladium

An intriguing question arises with dispersed metals: Will deactivation depend on the metal area or size of the metallic particles? Previous results (6) favored the idea that cyclopentane hydrogenolysis on palladium is insensitive to metallic dispersion in the absence of impurities. When using the parallel scheme we implicitly assume that hydrogenolysis and self-poisoning are connected; it was therefore interesting to determine the influence of palladium dispersion on k_d.

The deactivation constant

$$k_d = k_e \cdot kW/(C_A)^2 F_{A_0}$$

was measured on a series of catalysts for which the palladium dispersion was varied from 28 to 100%. The results are reported in Table 3.

The catalytic activity per surface palladium atom or turnover number for hydrogenolysis is found to be rather constant as a function of the palladium dispersion. The rate constant of deactiv:

TABLE 3

Influence of the Dispersion of Palladium on the Deactivation Constant and
Turnover Number of Pd/Al$_2$O$_3$ Catalysts at 290°C

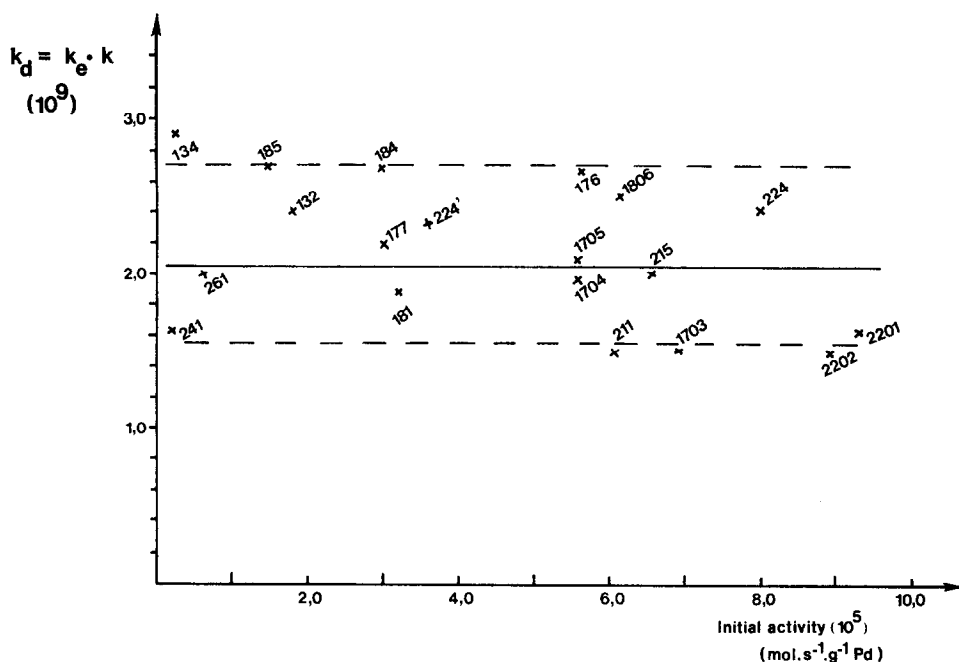| Catalyst	Pd (%)	Dispersion (%)	k_e	(10^7 mol·s^{-1}·g^{-1} of cat) Initial activity	$10^9 \cdot k_e \cdot k$ ($k_d = k_e \cdot k$)	Turnover number for hydrogenolysis
132	1.2	46	0.015	2.5	3.7	18
185	1.0	28	0.018	1.5	2.7	21
184	1.0	40	0.009	3.0	2.7	28
176	1.0	80	0.005	5.3	2.7	24
211	0.5	100	0.005	3.0	1.5	24
215	0.5	95	0.006	3.3	2.0	26.5
1703	1.0	80	0.002	7.0	1.4	33
2201	0.25	100	0.007	2.3	1.6	33
2202	0.25	90	0.0065	2.2	1.4	35
1806	1.00	40	0.009	2.5	2.3	24

FIG. 3. Plot of $k_e \cdot k$ against initial catalytic activity for a series of Pd/Al_2O_3 samples, at 290°C; pressure of cyclopentane, 100 Torr; weight of sample, 50 mg.

tion k_d which is proportional to $k_e \cdot k$ is also constant to a first approximation, since the variation is small when the palladium dispersion is varied over a broad range.

As activity is proportional to the palladium area, we can plot the deactivation constant against activity for a series of catalysts. Figure 3 reports the results obtained in that procedure. The remarkable point is that a change in activity by a factor of 100 gives a twofold variation of k_d. Moreover, a statistical distribution around a mean value is obtained.

This supports the idea that deactivation does not depend on the palladium dispersion. Deactivation and hydrogenolysis of cyclopentane are insensitive to particle size when this size, as measured by chemisorption or electron microscopy, is varied from 12 to more than 80 Å.

3. Influence of Sulfate Contamination

It is known that sulfate contamination of platinum (14) and palladium (6)

catalysts yields a selective poisoning of hydrogenolysis when the reduction is carried out at 400°C. This can be shown by an increase of the ratio of the activity for hydrogenation (A_1) to the activity for hydrogenolysis (A_2) on contaminated catalysts. By contrast, a reduction at 300°C yields a nonselective poisoning since both activities are suppressed in equal proportions. It was therefore interesting to investigate the influence of sulfur on deactivation. A drastic poisoning can change the form of the deactivation law since a linear decay of catalytic activity as a function of time can be observed at high sulfur levels. In order to compare different samples under similar conditions, we selected those experiments in which a homographic law is obeyed. The results are summarized in Table 4 in which chemical compositions, conditions of reduction, and catalytic properties are reported.

After reduction at 300°C, the deactivation rate constants measured on sulfate-

TABLE 4

Influence on Sulfate Contamination on Palladium Catalysts Reduced at 300 and 400°C on
Specific Catalytic Activities and Deactivation Rate Constant[a]

Sample	Chemical composition (wt%)		Temperature of reduction (°C)	Activity A_1 for cyclopentane at 290°C	Activity A_2 for benzene at 140°C	$R = A_1/A_2$	Deactivation rate constant
	Pd	S					
2201	0.25	—	300	9.3	100	10.7	1.6
184	1	—	400	3.0	28	9.4	2.7
321	0.35	0.2	300	8.0	87	11	2.1
311	0.35	0.1	300	6.7	90	13	1.3
205	1	0.1	400	1.08	22	20	1.0
202	1	0.1	400	0.85	20	24	1.0
332	0.25	0.4	400	0.08	2.5	31	0.6

[a] Catalytic activity expressed as moles per second per gram of Pd $\times 10^5$; deactivation rate constant expressed as $10^9 k_e \cdot k$ for a sample size of 50 mg.

contaminated samples are not significantly different from that of clean palladium catalysts. The selectivity ratios A_1/A_2 do not differ much either.

After reduction at 400°C a lower value is obtained for sulfate-containing catalysts. Sulfur suppresses hydrogenolysis and stabilizes the catalytic activity. This is an indication that hydrogenolysis and deactivation are two parallel reactions, and *a posteriori* this gives a justification of the hypothesis adopted as a basis of the kinetic scheme.

The decay of catalytic activity during the hydrogenolysis of cyclopentane on palladium catalysts can therefore be analyzed using the mathematical model proposed by Levenspiel *et al.* (2–4). The rate constant measured by this procedure does not change with palladium dispersion, and deactivation may be therefore considered as insensitive to the particle size of the metal. However, the rate constant is sensitive to poisoning, and this is consistent with the variations of catalytic activity observed in hydrogenolysis.

ACKNOWLEDGMENT

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